

Supporting Information

Stimulated X-ray Raman and Absorption Spectroscopy of Iron-Sulfur Dimers

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1 Active space of $[2\text{Fe-2S}]$ dimers

The 36 active orbitals are shown in Fig. 1. They can be classified as follows: 1-8 (terminal S), 9-14 (bridge S), 15-24 (3d of Fe), and 25-36 (4s or 4d of Fe).

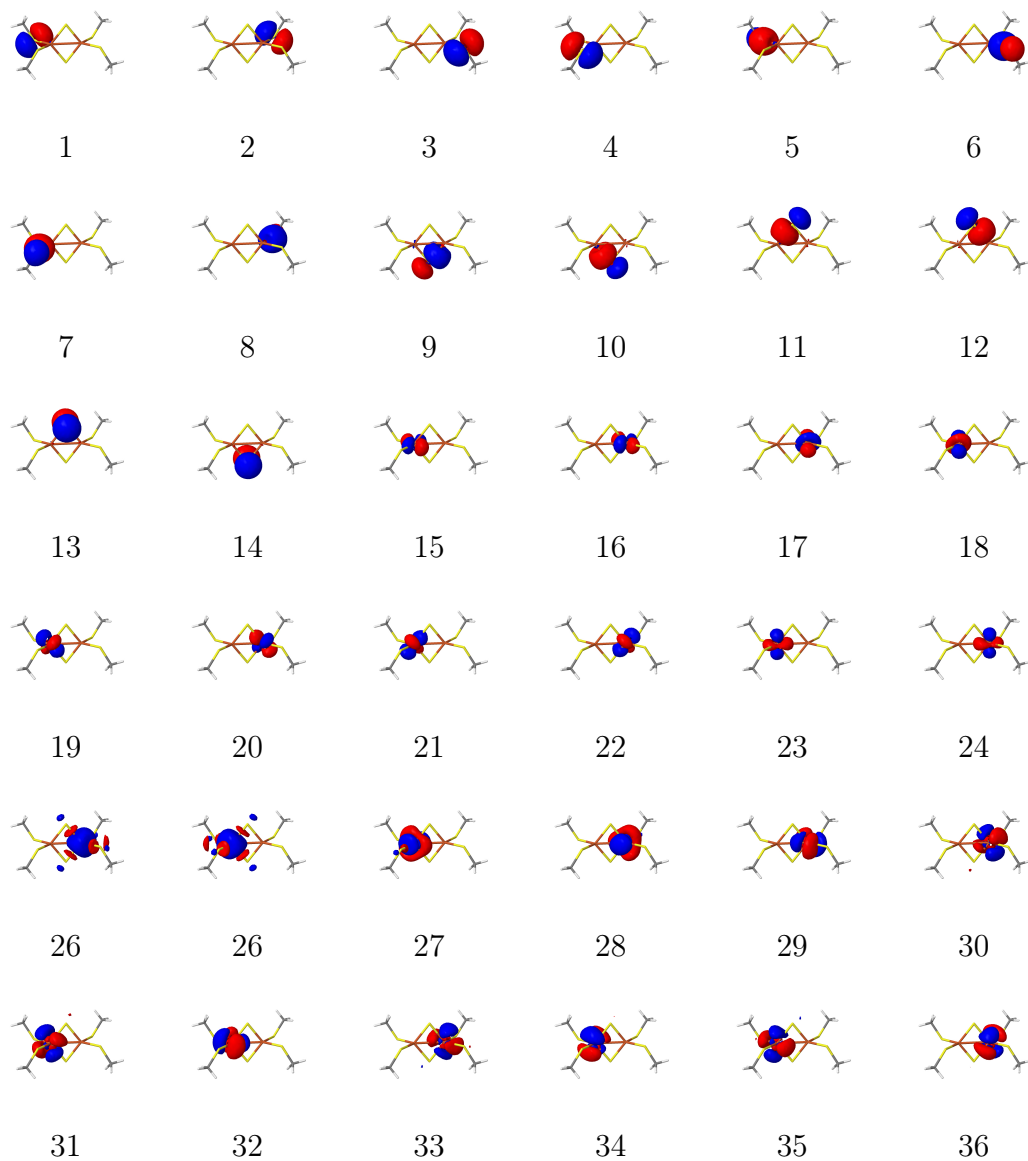


Figure 1: Active orbitals of $[2\text{Fe-2S}]$ dimers.

2 Charge density difference

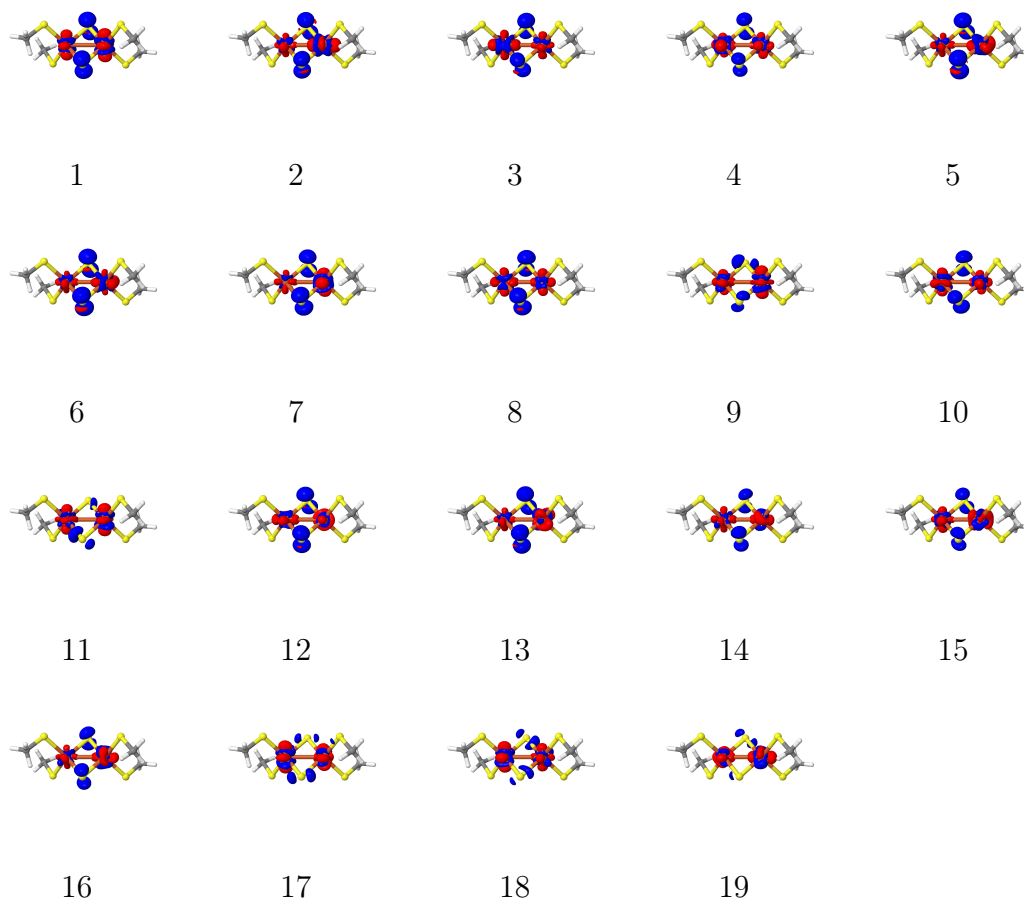


Figure 2: Charge density difference between excited states ($S = 0$) and the ground state of the $[2\text{Fe(III,III)}-2\text{S}]$ complex

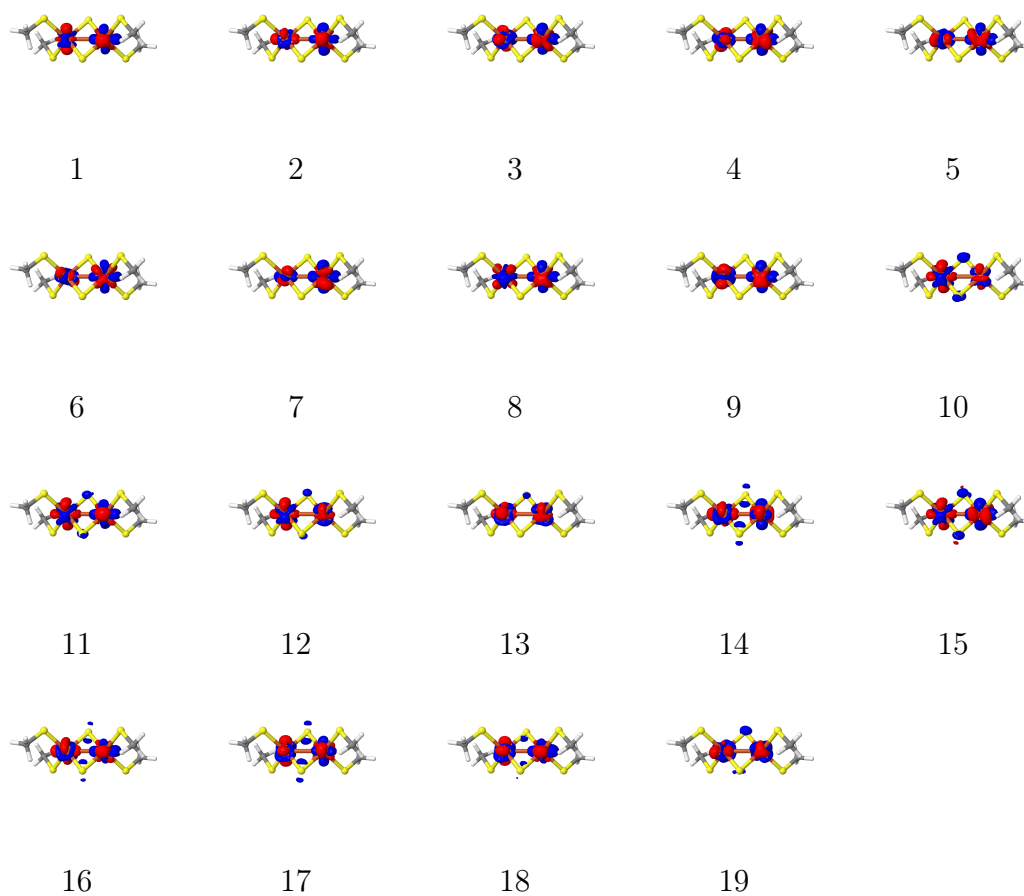


Figure 3: Charge density difference between excited states ($S = 1/2$) and the ground state of the [2Fe(III,II)-2S] complex.

3 Transition charge densities

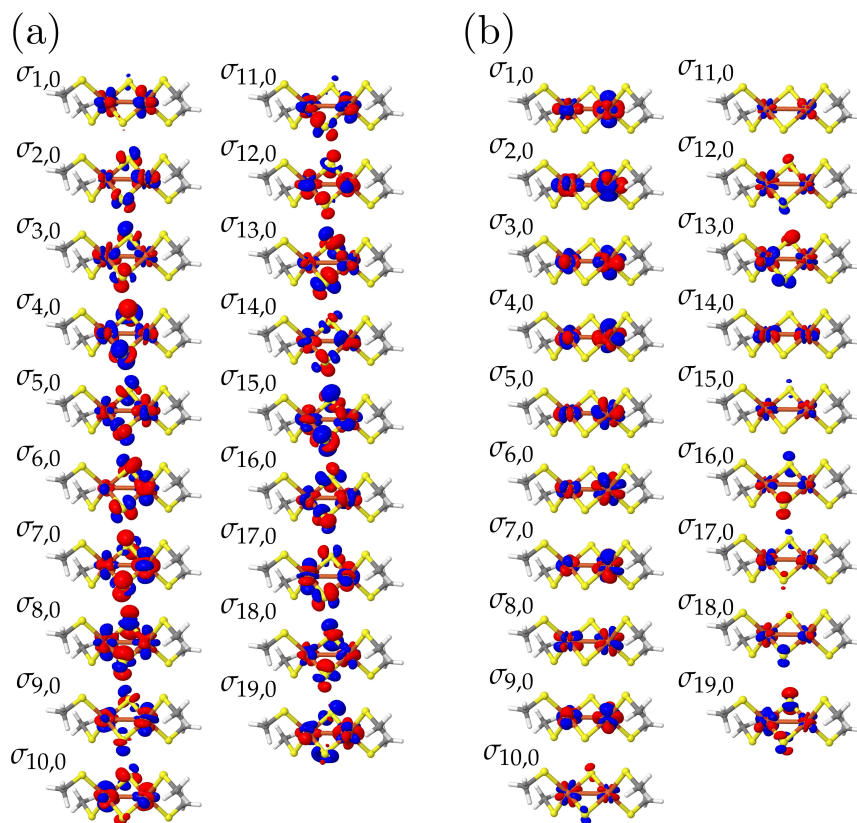


Figure 4: Transition charge density of respective electronic excitations of (a) the $[2\text{Fe(III,III)}-2\text{S}]$ complex and (b) the $[2\text{Fe(III,II)}-2\text{S}]$ complex.

4 Binatural/Natural transition orbitals

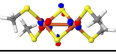
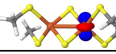
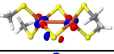
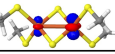
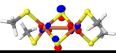

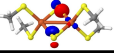
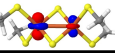
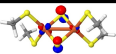
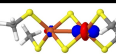
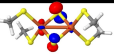
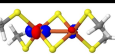
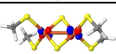
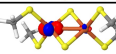
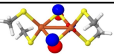
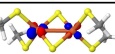
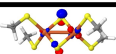
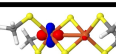
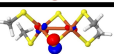
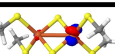
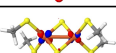
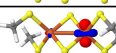
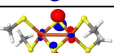
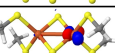
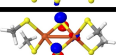
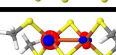
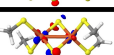
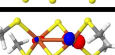
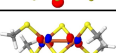
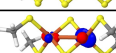
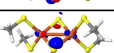
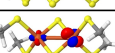
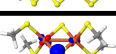
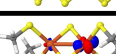
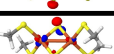
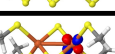
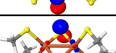
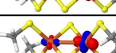
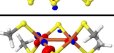
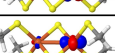
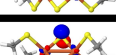
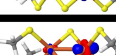
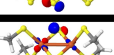
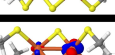
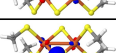
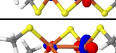
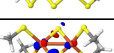
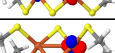
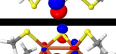
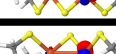
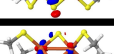
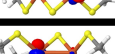
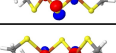
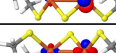
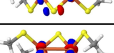
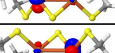
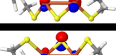
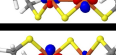
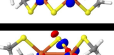
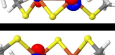
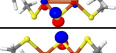
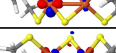
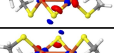
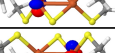
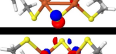
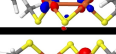
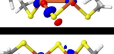
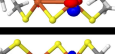
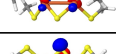
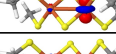
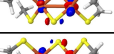
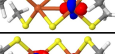
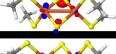
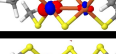
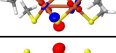
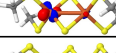
		HNTO	ENTO	Contrib.			HNTO	ENTO	Contrib.
S_1	1			0.642	S_{11}	1			0.711
	2			0.300		2			0.168
S_2	1			0.921	S_{12}	1			0.372
	2			0.069		2			0.264
S_3	1			0.865	S_{13}	1			0.469
	2			0.115		2			0.411
S_4	1			0.616	S_{14}	1			0.310
	2			0.229		2			0.273
S_5	1			0.461	S_{15}	1			0.411
	2			0.396		2			0.241
S_6	1			0.471	S_{16}	1			0.364
	2			0.450		2			0.321
S_7	1			0.710	S_{17}	1			0.743
	2			0.111		2			0.186
S_8	1			0.423	S_{18}	1			0.610
	2			0.250		2			0.218
S_9	1			0.657	S_{19}	1			0.458
	2			0.133		2			0.197
S_{10}	1			0.393					
	2			0.324					

Figure 5: Two dominant sets of HNTOs and ENTOS of respective electronic excitations of the $[2\text{Fe(III,III)}-2\text{S}]$ complex.

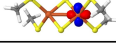
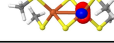
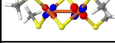
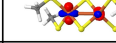
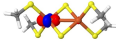
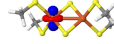
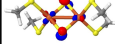
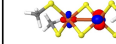
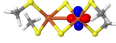
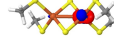
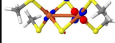
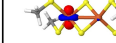
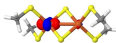
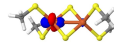
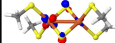
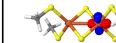
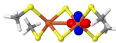
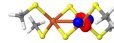
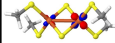
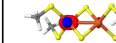
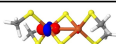
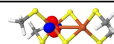
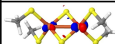
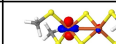
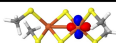
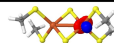
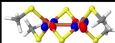
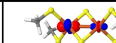
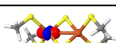
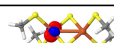
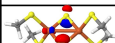
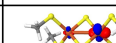
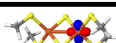
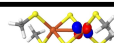
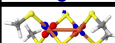
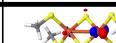
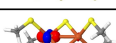
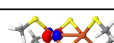
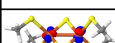
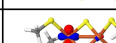
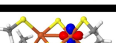
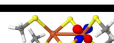
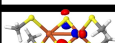
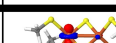
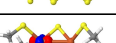
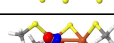
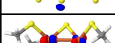
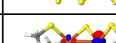
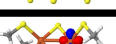
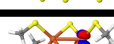
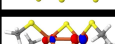
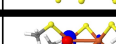
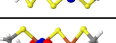
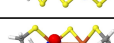
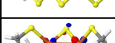
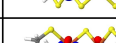
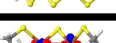
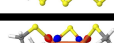
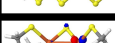
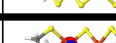
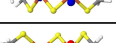
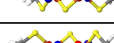
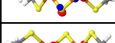
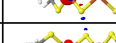
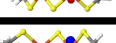
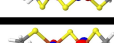
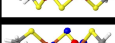
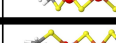
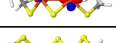
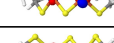
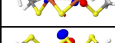
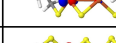

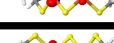
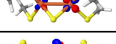
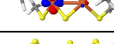
		HNTO	ENTO	Contrib.			HNTO	ENTO	Contrib.
D_1	1			0.811	D_{11}	1			0.662
	2			0.179		2			0.312
D_2	1			0.786	D_{12}	1			0.903
	2			0.156		2			0.083
D_3	1			0.814	D_{13}	1			0.884
	2			0.167		2			0.097
D_4	1			0.874	D_{14}	1			0.776
	2			0.114		2			0.132
D_5	1			0.833	D_{15}	1			0.580
	2			0.165		2			0.302
D_6	1			0.914	D_{16}	1			0.525
	2			0.085		2			0.386
D_7	1			0.933	D_{17}	1			0.858
	2			0.065		2			0.086
D_8	1			0.674	D_{18}	1			0.558
	2			0.322		2			0.339
D_9	1			0.749	D_{19}	1			0.900
	2			0.241		2			0.070
D_{10}	1			0.911					
	2			0.078					

Figure 6: Two dominant sets of HNTOs and ENTOs of respective electronic excitations of the $[2\text{Fe(III,II)}]\text{-2S}$ complex.